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WADD TECHNICAL REPORT 60-782
PART V

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VAPORIZATION OF COMPOUNDS AND ALLOYS
AT HIGH TEMPERATURE

PART V. MASS SPECTROMETRIC STUDY OF GASEOUS MOLECULES
ABOVE THE AgSn, AuSn, AND CuSn ALLOYS

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1960 to March 1961.

WADD Technical Report 60-782, Part I and Part II, have already been published, Part III and Part VI are in preparation, with Part IV to follow when it becomes available.

The authors wish to acknowledge the considerate encouragement and aid of Professor Paul Goldfinger.

ABSTRACT

The molecules AgSn, AuSn, and CuSn have been identified.

Dissociation energies have been measured to be:

$$D_0^{\circ}(\text{Sn}_2) = 45.8 \pm 4 \text{ kcal/mole}$$

$$D_0^{\circ}(\text{AgSn}) = 31.6 \pm 5 \text{ kcal/mole}$$

$$D_0^{\circ}(\text{AuSn}) = 57.5 \pm 4 \text{ kcal/mole}$$

$$D_0^{\circ}(\text{CuSn}) = 41.4 \pm 4 \text{ kcal/mole}$$

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RANKE

Chief, Ceramics and Graphite Branch
Directorate of Materials and Processes

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INTRODUCTION

The symmetric diatomic molecules Cu_2 , Ag_2 , Au_2 and Sn_2 have been studied previously. Sn_2 has been identified by Honig (1) and the dissociation energy calculated by Drowart and Honig (2). Cu_2 , Ag_2 and Au_2 have been identified by Kleman, Lindkvist and Selin (3) and by Ruamps (4) using optical spectroscopy. The dissociation energies of these three molecules have been measured mass spectrometrically by Drowart and Honig (2), by Schissel (5) and by Ackerman, Stafford and Drowart (6).

The asymmetric molecules AgCu and AuCu were observed spectroscopically by Ruamps (7). In addition AuCu was observed mass spectrometrically by Schissel (5). The dissociation energies of all three asymmetric molecules were determined mass spectrometrically by Ackerman (8) and Ackerman, Stafford and Drowart (6).

The dissociation energies of the symmetric and asymmetric molecules in the Cu, Ag, and Au triad were found to be related by Pauling's electronegativity relation (9). In this study alloys of Sn with Cu, Ag or Au were chosen to test this relation in the case of intermetallic gaseous molecules formed from atoms with different electronic structures.

The three molecules AgSn , AuSn and CuSn have not been

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observed previously. The present paper reports a mass spectrometric determination of the dissociation energies of these molecules and a verification of that of Sn_2 . Special care has been taken to insure that the values reported now and previously (6) are as accurate as possible relative to one another.

EXPERIMENTAL.

The three binary alloys were prepared by mixing together weighed quantities of the 99 % pure metals and melting them in situ in the mass spectrometer. The initial compositions of the alloys Ag-Sn, Au-Sn and Cu-Sn were about 0.9, 0.3 and 0.5 atom fraction of tin. Ag and Sn evaporated almost quantitatively from the Ag-Sn and the Au-Sn alloys respectively, while Cu-Sn formed a constant boiling mixture.

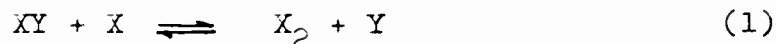
The experimental arrangement was identical to that used previously (6). The alloys were vaporized from a mullite cell contained in a molybdenum crucible. The ratio of the effusion orifice to the vaporizing surface was approximately 1/50. The brightness temperature of a black body hole in the base of the cell was measured with a Leeds and Northrup disappearing filament optical pyrometer.

Ions were formed from the effusing molecular beam by a 3 to 30 Amp. beam of 70 ev electrons, and then accelerated

to 2000 ev. Mass analysis was effected by a 20 cm radius of curvature, 60° sector, single focusing spectrometer. Ions were detected by a Ag-Mg secondary electron multiplier and a vibrating reed amplifier feeding a pen recorder.

EXPERIMENTAL DATA.

In addition to the atoms and to the molecules observed previously including Sn_3 and Sn_4 (1), only AgSn , AuSn and CuSn were observed. Information was obtained to calculate enthalpy changes for reactions :



The data are presented in Table I, in which all ionic intensities are corrected using the relative ionization cross sections and multiplier efficiencies given in Table II.

In addition, the ratio $\text{Sn}_2^+/\text{Sn}^+$ over pure tin was measured in the temperature range 1472-1769° K.

In the course of the experiments discrepancies appeared which could have been due either to an incorrect vapor pressure and heat of sublimation of tin or to an incorrect value for the relative ionization cross section of tin. The vapor pressure of tin was first determined. The heats of sublimation calculated from both the measured vapor pressure and from the temperature dependance of the vapor pressure between 1190°-1572°K were in agreement within 0.5 kcal/g.atom with the value $\Delta H^\circ_{298} = 72.00$ kcal/g.atom given

by Stull and Sinke⁽¹⁰⁾. The relative ionization cross section subsequently was measured relative to copper, gold and silver as explained earlier⁽⁶⁾. Relative to all three elements, the cross section was found to be about three times higher than that calculated⁽¹¹⁾. The best average relative cross section obtained is $\sigma(\text{Sn}) = 63$.

TREATMENT OF DATA.

Enthalpy changes for the reactions Eq.(1) were calculated from the data using the following equation :

$$\Delta H_0^\circ = -RT \ln \frac{I(Y^+)I(X_2^+)\sigma_Y(XY)\sigma_Y(X)}{I(XY^+)I(X^+)\sigma_Y(Y)\sigma_Y(X_2)} - T \Delta \left[(F^\circ - H_0^\circ)/T \right] \quad (2)$$

where $I(X^+)$ is the ion current due to species X ; $\sigma_Y(X)$ is the product of ionization cross section and relative multiplier efficiency; and $(F^\circ - H_0^\circ)/T$ the free energy function calculated according to the usual formulae⁽¹²⁾. The molecular constants used to calculate the free energy functions are shown in Table III. The multiplicity of Sn_2 was assumed (2) to be 3 and that of the three asymmetric molecules to be 2.

RESULTS AND DISCUSSION.

Table IV summarizes the values of the dissociation energies of interest in the present work, including those determined previously for Cu_2 , Ag_2 and Au_2 ⁽⁶⁾.

The dissociation energies at 0°K, D_0° , of AgSn , AuSn

and CuSn are calculated to be 31.6 ± 5 , 57.5 ± 4 and 41.4 ± 4 kcal/mole respectively. The greater part of the uncertainty is that in the free energy functions and is discussed in the following paper. No other data are available for comparison.

$D_0^\circ(\text{Sn}_2)$ calculated from the present data is 45.8 ± 4 kcal/mole. That calculated from Honig's data at 1200°K is 47.7 ± 4.5 kcal/mole. The dissociation energy of Sn_2 was obtained also from the temperature variation of the equilibrium constant for the reaction $\text{Sn}_2(\text{g}) \rightleftharpoons 2 \text{Sn}(\text{g})$. The value obtained was $D_{1600}^\circ = 59 \pm 10$ kcal/mole or $D_0^\circ = 52$ kcal/mole.

The measured D_0° of the asymmetric molecules XY may be compared with those of the symmetric molecules using the following equation due to Pauling.

$$D(\text{XY}) = 1/2 \left\{ D(\text{X}_2) + D(\text{Y}_2) \right\} + \Delta \quad (3)$$

where Δ is defined as proportional to the square of the electronegativity difference $23 \left[\chi(\text{X}) - \chi(\text{Y}) \right]^2$ where the D are single bond energies. Under the assumption that only one electron of the group IB atoms is effective in the bonding, D becomes equal to the measured D_0° for all the molecules studied except Sn_2 . The molecule Sn_2 , a congener of C_2 , presumably is double bonded and the single bond energy $D(\text{Sn} - \text{Sn})$ is estimated⁽¹²⁾ to be 35 kcal/mole from the lattice energy of gray tin.

Numerical values of the three terms in Eq.(3) are given in columns 2, 3 and 4 of Table V. The calculated differences in electronegativity are shown in the fifth column and are seen, except for AgSn, to agree with the values calculated from heats of formation of various salts. These literature values⁽⁹⁾ are Sn(1.6), Cu(1.8) and Au(2.4). The negative Δ for AgSn, which is just on the limit of being experimentally significant seems to be an exception to Pauling's rule.

Previously, a qualitative correlation between the quantity Δ and the heat of mixing of two liquid metals had been noted⁽⁶⁾. In the present case the correlation is complicated by the large differences both of crystal structure and of valence between the IB metals and Sn, invalidating the quasi-chemical model. The curves $\Delta H(\text{mix})$ VS. mole fraction for AgSn and CuSn are irregular showing approximately equal maxima for Sn poor alloys, but the formation of AgSn is endothermic for $n(\text{Sn}) \approx 0.8$. The formation of AuSn alloys from the pure metals however is always more exothermic than that of either AgSn or CuSn, in general accordance with the values of Δ given in Table V.

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TABLE Ia. Corrected dimer/monomer ratios and calculated dissociation energies from ion intensities above pure tin.

Exp.	T°K	$(P_{\text{Sn}}/P_{\text{Sn}_2}) \times 10^{-2}$	D_0°
0305.6	1472	4.50	45.9
8	1520	2.60	47.0
5	1533	2.95	46.5
7	1558	2.60	46.5
1	1568	4.75	44.6
4	1545	3.00	45.2
9	1647	2.36	46.1
3	1693	2.23	45.6
10	1706	2.05	45.8
2	1759	2.26	45.2
11	1769	1.97	45.4
Mean			45.8

TABLE Ib. Decimal logarithms of the equilibrium constant K for the reaction and dissociation energies from corrected ion intensities measured above the alloys.

Exp.	T°K	- log K (a)	D ₀ ⁰ (XY)	Symmetric molecules of reference (X ₂)
AgSn				
0305.1	1568	-0.226	31.4	Ag ₂
2	1759	-0.332	30.2	
0305.1	1568	-1.58	32.7	Sn ₂
2	1759	-1.61	32.1	
mean			31.6	

continued

$$(a) K = \frac{I(X_2^+)I(Y^+)\sigma_Y(XY)\sigma_X(X)}{I(XY^+)I(X)\sigma_X(X_2)\sigma_Y(Y)}$$

TABLE Ib : (continued)

Exp.	T°K	- log K	D _O ^o (XY)	symmetric molecule of reference
AuSn				
0307.9	1686	1.41	57.4	Au ₂
16	1723	1.33	57.0	
8	1732	1.51	58.4	
1	1739	1.23	56.2	
4	1759	1.49	58.4	
2	1785	1.30	57.1	
15	1787	1.60	59.5	
3	1835	1.37	55.9	
10	1843	1.36	57.8	
14	1865	1.37	58.1	
11	1879	1.31	57.6	
13	1890	1.33	57.8	
12	1928	1.25	57.3	
0313.8	1815	1.70	60.5	
2	1821	1.08	55.5	
7	1867	1.46	58.8	
4	1878	1.13	56.1	
6	1898	1.39	58.4	
3	1966	1.01	55.4	
5	1987	1.20	57.1	
			mean	57.5

.../...

TABLE Ib : (continued)

Exp.	T°K	- log K	$D_0^0(XY)$	symmetric molecule of reference
CuSn				
0306.3	1730	-0.098	42.7	Sn ₂
5	1758	-0.206	41.7	
2	1764	-0.122	42.4	
1	1785	-0.221	41.3	
6	1798	-0.233	41.4	
7	1834	-0.217	41.4	
0314.2	1632	-0.225	43.1	
3	1673	-0.004	44.7	Cu ₂
4	1772	-0.129	43.3	
5	1852	-0.116	43.1	
0306.3	1730	-0.031	39.7	
5	1758	0.073	40.4	
2	1764	0.029	40.1	
1	1785	0.059	39.3	
6	1798	-0.005	39.8	
7	1834	-0.145	38.6	
mean			41.4	

.../...

TABLE II. Relative ionization cross sections and multiplier yields.

Species	Ionization cross section, σ	Mult. yield x cross section, $\sigma\gamma$
Cu	18.4 (a)	18.4
Ag	34.8 (a)	24.9
Au	39	17
Sn	63	43
Cu ₂	37 (b)	28
Ag ₂	70	34
Au ₂	78	28
Sn ₂	126	56
AgSn	98	43
AuSn	102	40
CuSn	82	42

(a) see ref. 11.

(b) for molecules : $\sigma(XY) = \sigma(X) + \sigma(Y)$

TABLE III. Molecular constants used to calculate the
free energy functions.

Molecules	Internuclear distance (Å)	Vibration frequencies (cm ⁻¹)
Sn ₂	2.80	300
AgSn	2.76	192
AuSn	2.69	200
CuSn	2.58	213

TABLE IV. Dissociation energies at 0°K in kcal/mole of certain diatomic molecules containing Ag, Au, Cu and Sn.

Ag ₂	37.6 (a)	AgSn	31.6 ± 5
Au ₂	51.5 (a)	AuSn	57.5 ± 4
Cu ₂	45.5 (a)	CuSn	41.4 ± 4
Sn ₂	45.8 (b)		

(a) from ref. 6

(b) third law result, this work; second law result 52 ± 10 kcal/mole; the values calculated from Honig's data (ref. 1) is 47.7 ± 4.5 .

TABLE V. Comparison of $D(XY)$ with
 $1/2 \left[D(X_2) + D(Y_2) \right]$. (kcal/mole)

molecules	$D(XY)$ (a)	$1/2 \left[D(X_2) + D(Y_2) \right]$ (a)	Δ	$\sqrt{\Delta/23}$
AgSn	31.6	36.3	- 5	-
AuSn	57.5	43.3	+ 14	0.8
CuSn	41.4	40.3	+ 1	0.2

(a) D is taken equal to the measured D_0^0 , except in the case of Sn_2 , where it is taken as 35 kcal/mole (ref. 12).